

PREPARATION OF MOLECULAR SIEVES INVOLVING SPRAY DRYING

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Field of the Invention

The present invention relates to a process for producing crystalline molecular sieves, including zeolites, employing a spray drying step.

Background

Molecular sieves are a commercially important class of crystalline materials. They have distinct crystal structures with ordered pore structures which are demonstrated by distinct X-ray diffraction patterns. The crystal structure defines cavities and pores which are characteristic of the different species. Natural and synthetic crystalline molecular sieves are useful as catalysts and adsorbents. The adsorptive and catalytic properties of each molecular sieve are determined in part by the dimensions of its pores and cavities. Thus, the utility of a particular molecular sieve in a particular application depends at least partly on its crystal structure. Because of their unique sieving characteristics, as well as their catalytic properties, molecular sieves are especially useful in such applications as gas drying and separation and hydrocarbon conversion. The term "molecular sieve" refers to a material prepared according to the present invention having a fixed, open-network structure, usually crystalline, that may be used to separate hydrocarbons or other mixtures by selective occlusion of one or more of the constituents, or may be used as a catalyst in a catalytic conversion process. Zeolites are included in the term "molecular sieve".

Prior art methods of preparing crystalline zeolites typically produce finely divided crystals which must be separated from an excess of liquid in which the zeolite is crystallized. The liquid, in turn, must be treated for reuse or else be discarded, with potentially deleterious environmental consequences. Preparing commercially useful catalytic materials which contain the powdered zeolite also normally requires additional binding and forming steps. Typically, the zeolite powder as crystallized must be mixed with a binder material and then formed into shaped particles or agglomerates, using methods such as extruding, agglomeration, and the like.

01 These binding and forming steps greatly increase the complexity of catalyst manufacture
02 involving, e.g., zeolitic materials. The additional steps may also have an adverse effect on the
03 catalytic performance of the zeolite so bound and formed.

04 A number of processes have been offered for preparing crystalline zeolites within
05 discrete particles. For example, Howell, et al., in U. S. Patent No. 3,119,660 teaches a method
06 for producing crystalline metal aluminosilicate zeolite by reacting preformed bodies of clay
07 particles in an aqueous reactant mixture including alkali metal oxide. Similar processes for
08 preparing zeolites from formed bodies, which may contain zeolitic seed crystals, in alkali
09 solutions are also taught in U. S. Patent No. 4,424,144 to Pryor, et al., U. S. Patent No.
10 4,235,753 to Brown, et al., U. S. Patent No. 3,777,006 to Rundell, et al., U. S. Patent No.
11 3,119,659 to Taggart, et al, U.S. Patent No. 3,773,690 to Heinze, et al., U.S. Patent No
12 4,977,120 to Sakurada, et al. and GB 2 160 517 A. U.S. Patent No. 3,094,383 teaches a method
13 of forming an A type zeolite by aging a homogeneous reaction mixture out of contact with an
14 external aqueous liquid phase but under conditions to prevent the dehydration of the mixture.
15 GB 1 567 856 discloses a method of preparing zeolite A by heating an extruded mixture of
16 metakaolin powder and sodium hydroxide.
17

18
19
20 In U. S. Patent No. 4,058,586, Chi, et al. discloses a method for crystallizing zeolites
21 within formed particles containing added powdered zeolite, where the formed particles furnish
22 all of the liquid needed for crystallization. Crystallizing the particles in an aqueous alkaline
23 solution is not required using the process of Chi, et al.

24 Verduijn, in WO 92/12928, teaches a method of preparing binder-free zeolite aggregates
25 by aging silica-bound extruded zeolites in an aqueous ionic solution containing hydroxy ions.
26 According to the disclosure of Verduijn, the presence of zeolite crystals in the extrudate is
27 critical for making strong crystalline zeolite extrudates. Verduijn, et al., in EPO A1/0,284,206,
28 describe a method of preparing binderless zeolite L by forming silica and preferably 10-50 wt %
29 performed zeolite L crystallites into particles, and then reacting the particles with an alkaline
30 solution containing a source of alumina to form the zeolite L.
31

32 More recently, similar methods have been proposed for preparing high silica zeolitic
33 materials. Conventional methods for preparing high silica materials, having a $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar
34

01 ratio of greater than about 10, and more typically greater than about 20, typically involves
02 crystallizing the zeolites from aqueous solution. For example, U.S. Patent No. 3,702,886 to
03 Argauer, et al., teaches a method of preparing ZSM-5 from a solution containing tetrapropyl
04 ammonium hydroxide, sodium oxide, an oxide of aluminum or gallium, an oxide of silica or
05 germanium, and water. The digestion of the gel particles is carried out until crystals form. The
06 crystals are separated from the liquid and recovered.

07
08 EPO A2/0,156,595, discloses the preparation of crystalline zeolites having a silica to
09 alumina mole ratio greater than 12 and a Constraint Index of 1 to 12 by forming a mixture of
10 seed crystals, a source of silica, a source of alumina and water into shaped particles, which are
11 then crystallized in an aqueous reaction mixture containing a source of alkali cations. It is also
12 taught that alumina-containing clay may be used as an alumina source. U.S. Patent
13 No. 4,522,705 is directed to a catalytic cracking catalyst comprising an additive prepared by the
14 in-situ crystallization of a clay aggregate disclosed in EPO A2/0,156,595.

15
16 Special methods for preparing the reaction mixture from which a zeolite may be
17 crystallized have also been proposed. In U.S. Patent No. 4,560,542 a dried hydrogel containing
18 silica and alumina is contacted with a fluid medium containing an organic templating agent and
19 maintained at specified crystallization conditions to form a crystalline aluminosilicate. In U.S.
20 Patent No. 5,240,892 a reaction mixture containing at least about 30 weight percent solids
21 content of alumina and precipitated silica is taught for preparing zeolites. The method of
22 preparing the reaction mixture allows agitation of the mixture during crystallization, in spite of
23 the high solids content of the mixture.

24
25 Zeolite crystallization from reaction mixtures initially containing a gel-like phase in
26 equilibrium with an excess of liquid phase is disclosed in R. Aiello, et al., "Zeolite
27 Crystallization from Dense Systems", *Materials Engineering* 1992, Vol. 3, n. 3, pp.407-416.

28
29 Other approaches to synthesis of crystalline zeolites have included preparing the zeolites
30 in an essentially aqueous-free environment. These non-aqueous methods have been described,
31 for example, in *ZEOLITES*, 1992, Vol. 12, April/May, p. 343; *ZEOLITES* 1990, Vol. 10,
32 November/December, p. 753; *ZEOLITES* 1989, Vol. 9, November, p. 468; *Nature*, Vol.
33 317(12), September 1985, p. 157; and *J. Chem. Soc., Chem. Commun.*, 1988, p. 1486. *J. Chem.*
34

01 *Soc., Chem. Commun.*, 1993, p. 659 describes a kneading method for synthesizing ZSM-35 in a
02 nonaqueous system, in which the amount of liquids used to prepare a crystallization mixture is
03 not sufficient to wet all the solid particles so that the conglomerate reactant is actually a mixture
04 of dry powder and small doughy lumps.

05 U. S. Patent No. 6,004,527, issued December 21, 1999 to Murrell et al. relates to the
06 hydrothermal synthesis of large pore molecular sieves from nutrients, at least one of which
07 contains an amorphous framework-structure, and which framework-structure is essentially
08 retained in the synthetic molecular sieve. The synthesis involves impregnating a cation oxide
09 framework comprising a first cation oxide with a liquid containing a second cation different
10 from the first cation, said liquid being free of a pore forming agent. The impregnated cation
11 oxide framework is dried and impregnated again with a liquid containing a pore forming agent.
12 The amount of liquid containing the pore forming agent in the second impregnation does not
13 exceed the incipient wetness point of the cation oxide framework. The impregnated cation
14 oxide framework is then heated to produce a large pore molecular sieve.

15 U. S. Patent No. 5,558,851, issued September 24, 1996 to Miller, discloses a method for
16 preparing a crystalline zeolite from a reaction mixture containing only enough water so the
17 reaction mixture can be shaped if desired. The reaction mixture is heated at crystallization
18 conditions and in the absence of an external liquid phase, so that excess liquid need not be
19 removed from the crystallized material prior to drying the crystals.

20 U. S. Patent No. 4,091,007, issued May 23, 1978 to Dwyer et al., discloses a method for
21 preparing a crystalline aluminosilicate zeolite having uniform pores and greater than 40 percent
22 crystallinity which comprises forming a critical reaction mixture containing a source of at least
23 two cations, silica, alumina and water, wherein at least about 70 weight percent of the alumina is
24 provided to the reaction mixture by an alumina-containing clay being added thereto. The
25 reaction mixture is maintained at a temperature and pressure for a time necessary to crystallize
26 the crystalline aluminosilicate. It is stated that it is desirable to preform the reaction mixture
27 into discrete particles such as pellets or extrudates which retain their shape and acquire
28 substantial strength in the crystallization process.

01 In Example 22, Dwyer et al. discloses the synthesis of ZSM-5 by mixing Georgia kaolin,
02 Ludox colloidal silica and water. The mixture is dried in a Koline-Sanderson spray drier. More
03 than 30% of the spray dried particles are larger than 200 mesh. The particles are calcined in air,
04 and a portion of them mixed with a solution containing tetrapropylammonium bromide, NaOH
05 pellets, Q-brand sodium silicate, NaCl and water. The resulting mixture is transferred to a static
06 bomb and placed in a heated oil bath. Crystals are recovered and determined to be 50 weight
07 percent crystalline ZSM-5.
08

09 SUMMARY OF THE INVENTION

10 In accordance with the present invention, there is provided a method of preparing a
11 crystalline molecular sieve comprising:
12

- 13 a. forming an aqueous slurry comprising an active source of silicon oxide and an
14 organic templating agent capable of forming the molecular sieve;
- 15 b. spray drying the aqueous slurry to form particles;
- 16 c. heating the spray dried particles at a temperature and pressure sufficient to cause
17 crystallization of the molecular sieve.
18

19 Step c may be conducted in the absence of added water. The aqueous slurry may also contain
20 an active source of an alkali metal oxide and/or an active source of the oxides of aluminum,
21 boron, iron, gallium, indium, titanium, or mixtures thereof. The aqueous slurry may also
22 contain seed crystals of the molecular sieve. The molecular sieve may be a zeolite, such as
23 ZSM-5 or beta. The molecular sieve may have a mole ratio of silicon oxide to the oxides of
24 aluminum, boron, iron, gallium, indium, titanium, or mixtures thereof is greater than 12.
25

26 The present invention also provides a method of preparing a crystalline molecular sieve
27 comprising:

- 28 a. forming an aqueous slurry comprising an active source of silicon oxide and an
29 organic templating agent capable of forming the molecular sieve;
- 30 b. spray drying the aqueous slurry to form particles;
- 31 c. adding additional organic templating agent to the spray dried particles to form a
32 slurry; and
33
34

01 d. heating the slurry from step c at a temperature and pressure sufficient to cause
02 crystallization of the molecular sieve.

03 The aqueous slurry may also contain an active source of an alkali metal oxide and/or an
04 active source of the oxides of aluminum, boron, iron, gallium, indium, titanium, or mixtures
05 thereof. The aqueous slurry may also contain seed crystals of the molecular sieve. The
06 molecular sieve may be a zeolite, such as ZSM-5 or beta. The molecular sieve may have a mole
07 ratio of silicon oxide to the oxides of aluminum, boron, iron, gallium, indium, titanium, or
08 mixtures thereof is greater than 12.
09
10

11 DETAILED DESCRIPTION OF THE INVENTION

12

13 The reaction mixture from which the molecular sieve is crystallized is an aqueous slurry
14 and comprises at least one active source of silica, optionally an organic templating agent, and
15 optionally active sources of metal oxides.

16 The solids content of the reaction mixture will depend on the molecular sieve desired.
17 However, the reaction mixture should contain sufficient water such that, prior to spray drying,
18 the reaction mixture has a solids content of about 10-20 weight percent.
19

20 The molecular sieve made by the present process typically has a silica to alumina mole
21 ratio of greater than 12. Zeolites having a very high silica to alumina ratio are within the scope
22 of the process, including zeolites having a silica to alumina mole ratio greater than 100. Also
23 included are zeolites which are essentially aluminum-free. Especially when commercial silica
24 sources are used, aluminum is almost always present to a greater or lesser degree. Thus, by
25 “aluminum-free” is meant that no aluminum is intentionally added to the reaction mixture, e.g.,
26 as an alumina or aluminate reagent, and that to the extent aluminum is present, it occurs only as
27 a contaminant in the reagents.
28

29 The aqueous slurry may contain active sources metal oxides, such as the oxides of
30 aluminum, boron, iron, gallium, indium, titanium, or mixtures thereof .
31

32 Typical sources of silicon oxide (SiO_2) include silicates, silica hydrogel, silicic acid,
33 colloidal silica, fumed silica, tetraalkyl orthosilicates silica hydroxides, precipitated silica and
34 clays. Typical sources of aluminum oxide (Al_2O_3) when used in the reaction mixture include

01 aluminates, alumina, and aluminum compounds such as AlCl_3 , $\text{Al}_2(\text{SO}_4)_3$, aluminum hydroxide
02 ($\text{Al}(\text{OH}_3)$), kaolin clays, and other zeolites. Titanium, gallium, iron, boron and indium can be
03 added in forms corresponding to their aluminum and silicon counterparts. Salts, particularly
04 alkali metal halides such as sodium chloride, can be added to or formed in the reaction mixture.
05 They are disclosed in the literature as aiding the crystallization of zeolites while preventing
06 silica occlusion in the lattice.
07

08 An organic templating agent capable forming the zeolite is included in the reaction
09 mixture. Typically, the templating agent will be an organic compound which contains nitrogen
10 or phosphorus. The sources of organic nitrogen-containing cations may be primary, secondary
11 or tertiary amines or quaternary ammonium compounds, depending on the particular molecular
12 sieve product to result from crystallization from the reaction mixture. Non-limiting examples of
13 quaternary ammonium compounds include salts of tetramethylammonium,
14 tetraethylammonium, tetrapropylammonium, tetrabutylammonium,
15 dibenzyltrimethylammonium, dibenzyltriethylammonium, benzyltrimethylammonium and
16 2-(hydroxylalkyl) trialkylammonium, where alkyl is methyl, or ethyl or a combination thereof.
17 Non-limiting examples of amines useful in the present process include the compounds of
18 trimethylamine, triethylamine, tripropylamine, ethylenediamine, propanediamine,
19 butanediamine, pentanediamine, propanediamine, butanediamine, pentanediamine,
20 hexanediamine, methylamine, ethylamine, propylamine, butylamine, dimethylamine,
21 diethylamine, dipropylamine, benzylamine, aniline, pyridine, piperidine and pyrrolidine.
22 Amines useful herein are those having a pK_a in the range of between about 7 and about 12.
23
24

25 It has been found that the organic templating agent may be added in two manners. First,
26 all of the template can be added to the reaction mixture prior to spray drying. This has been
27 found to result in zeolites having good crystallinity. Alternatively, a portion of the template can
28 be added to the reaction mixture prior to spray drying, with the remainder of the template being
29 added to the spray dried material prior to reaction. It has been found that adding all of the
30 template to the spray dried material prior to reaction may result in no crystallization (see
31 Comparative Example H).
32
33
34

The reaction mixture may also comprise one or more active sources of alkali metal oxide. Sources of lithium, sodium and potassium, are preferred. Any alkali metal compound which is not detrimental to the crystallization process is suitable here. Non-limiting examples include oxides, hydroxides, nitrates, sulfates, halogenides, oxalates, citrates and acetates. According to the present process, a reaction mixture is prepared having a composition, in terms of mol

	<u>Broad</u>	<u>Preferred</u>
YO_2/W_aO_b	2 - ∞	12 - ∞
M^+/YO_2	0 - 1	0.04 - 0.7
R/YO_2	0 - 0.5	0.01 - 0.3
OH^-/YO_2	0.05 - 0.4	0.05 - 0.3
H_2O/YO_2	0.5 - 5	1 - 4

Y is silicon, germanium or both, W is aluminum, boron, iron, gallium, indium, titanium, or a mixture thereof, a is 1 or 2, b is 2 when a is 1 (i.e., W is tetravalent) and b is 3 when a is 2 (i.e., W is trivalent), M^+ is an alkali metal ion, preferably sodium, and R is a templating agent. The type of molecular sieve crystallized from the reaction mixture depends on a number of factors, including crystallization conditions, specific composition of the reaction mixture and the type of templating agent used.

In a preferred method of the present invention, a reaction mixture is formed containing one or more sources of alkali metal oxide, organic nitrogen-containing cations, hydrogen ions, an oxide of silicon, water, and optionally, an oxide of aluminum. In general, the reaction mixture will have a pH of at least 7, and preferably between about 8 and 14.

Once the aqueous slurry reaction mixture is formed, it is spray dried to form particles. Spray drying is a direct fired method of drying slurries or solutions, which is an extremely important process for producing microspheres for fluid bed or slurry catalysts or adsorbents as well as other applications. Spray drying involves feeding a well dispersed liquid-solid slurry or solution, often containing a binder, to an atomizer and subsequently flash drying in a stream of hot air. The atomizer can be of several different types. Most common is wheel atomization, which uses high speed rotation of a wheel or disc to break up the slurry into droplets that spin out from the wheel into chamber and are flash dried prior to hitting the chamber walls. The

01 atomization may also be accomplished by single fluid nozzles, which rely on hydrostatic
02 pressure to force the slurry through a small nozzle. Multi-fluid nozzles are also used, where gas
03 pressure is used to force the slurry through the nozzle. After drying, the heavier particles can be
04 collected at the bottom of the chamber, while smaller, lighter particles are collected in cyclones
05 and/or bag houses. Alternately, all particles can be collected in a bag house. The dry airflow
06 can be tangential, co-current or counter current depending on the design of the dryer.
07

08 In most fluid bed operations, particle size of the catalyst is an important factor and
09 generally requires an average particle size between 65 and 80 microns. A narrow particle size
10 distribution is also desirable with a range between 10 and 200 microns. It is important in most
11 operations to limit the amount of particles less than 20 microns to below 5 wt.% and above 150
12 microns to less than 5 wt.%. This facilitates catalyst-product separation, while at the same time
13 allowing good fluidization of the bed. Particle size can be controlled by nozzle size or wheel
14 speed and design as well as slurry solids content and viscosity, and also by the velocity and
15 direction of the air with respect to the atomizer.
16

17 Particle morphology is also important and is mostly controlled by the spray dryer
18 operation. It is important to avoid secondary atomization, impingement of fine dry particles on
19 wet droplets and blowholes in order to avoid non-spherical particles. The inlet temperature of
20 the drying air and slurry solids content can be varied to minimize blowholes, while secondary
21 atomization can be controlled by nozzle or wheel design. The impingement of small, dry
22 particles onto wet droplets can be minimized by correct control of air flow and direction and
23 minimizing secondary atomization.
24

25 Other important parameters, such as particle bulk density and hardness, are generally,
26 controlled by the feed slurry. While high density and particle hardness are for the most part
27 desirable, the particle can not be so dense that it inhibits fluidization nor so hard as to cause
28 erosion of equipment. The slurry particle size has the largest impact on density and hardness,
29 but type of binder and particle surface charge are also important factors.
30

31 Crystallization is conducted at an elevated temperature and usually in an autoclave so
32 that the reaction mixture is subject to autogenous pressure until the crystals of the molecular
33 sieve are formed. The temperatures during the hydrothermal crystallization step are typically
34

01 maintained from about 80°C. to about 200°C., preferably from about 90°C. to about 180°C. and
02 more preferably from about 100°C. to about 170°C.

03 Once the molecular sieve crystals have formed, the crystals may be water-washed and
04 then dried, e.g., at 90°C. to 150°C. for from 8 to 24 hours. The drying step can be performed at
05 atmospheric or subatmospheric pressures.
06

07 Crystalline material (i.e. "seed" crystals) may be added to the mixture prior to the
08 crystallization step, and methods for enhancing the crystallization of zeolites by adding "seed"
09 crystals are well known. However, the addition of seed crystals is not a requirement of the
10 present process. Indeed, it is an important feature of the present process that zeolites can be
11 crystallized within the reaction mixture in the absence of crystals added prior to the
12 crystallization step. When they are used, the seed crystals may be crystals of the desired
13 molecular sieve, or crystals of a different molecular sieve. When seed crystals are used, they
14 are typically added in an amount between 0.1 and 10% of the weight of YO₂, e.g. silica, used in
15 the reaction mixture.
16

17 In one general embodiment, the present method is applicable to the synthesis of zeolites
18 having a silica/alumina molar ratio greater than 12. In a more specific embodiment, the method
19 is useful for preparing silicate and aluminosilicate zeolites having a Constraint Index of greater
20 than about 1. The Constraint Index as used herein is defined in J. Catalysis 67, page 218 and
21 also disclosed in U.S. Patent No. 4,481,177.
22

23 Specific, non-limiting examples of crystalline zeolites which may be prepared by the
24 present method include ZSM-5, beta and other similar materials.
25

26 Zeolite ZSM-5 and the conventional preparation thereof are described in U.S. Patent
27 No. 3,702,886, the disclosure of which is incorporated herein by reference. The reaction
28 mixture from which ZSM-5 can be suitably prepared is formed by mixing sources of silica and
29 alumina with a templating agent, preferably tetrapropylammonium hydroxide, and sources of an
30 alkali metal oxide, preferably sodium oxide.
31

32 Zeolite beta and the conventional preparation thereof are described in U.S. Patent
33 No. 3,308,069, the disclosure of which is incorporated herein by reference. The reaction
34 mixture from which zeolite beta can be suitably prepared is formed by mixing sources of silica

01 and alumina with a templating agent, preferably tetraethylammonium hydroxide (TEAOH), and
02 sources of an alkali metal oxide, preferably sodium oxide. The crystallization procedures can be
03 satisfactorily carried out at temperatures within the range from about 75 °C to about 200°C.
04 Heating under autogenous pressure is carried out until desired crystalline zeolite product is
05 formed.

07 Zeolite boron beta and the conventional preparation thereof are described in U.S. Patent
08 Nos. 4,788,169 and 5,166,111, the disclosures of which are incorporated herein by reference.
09 Boron beta zeolites can be suitably prepared from a reaction mixture containing sources of an
10 alkali metal borate, a templating agent such as tetraethylammonium hydroxide or bis(1-azonia,
11 bicyclo[2.2.2]octane)- α , ω alkane diquatery ammonium ion, and an oxide of silicon or
12 germanium, or mixture of the two.

14 Sources of boron for the reaction mixture include borosilicate glasses and most
15 particularly, other reactive borates such as sodium borate and borate esters. Typical sources of
16 silicon oxide include precipitated silica, silicates, silica hydrogel, silicic acid, colloidal silica,
17 tetra-alkyl or/ho-silicates, and silica hydroxides.

19 EXAMPLES

20 The following examples illustrate the invention. The stoichiometry for the reaction
21 mixtures used in each example is shown in Table 2 below.

22 Example 1

23 154 pounds of deionized water (DI H₂O) and 35.6 pounds of a 35 %
24 tetraethylammonium hydroxide (TEAOH) solution was added to a 100 gallon Cowles dissolver.
25 The mixer was turned on and 44.9 pounds HiSil 233 (90% SiO₂, 10% H₂O) was added over 25
26 minutes. After the HiSil addition was complete, 3.8 pounds of sodium hydroxide (50 %
27 solution), 2.95 pounds of Versal 250 (75% Al₂O₃, 25% H₂O) and 2.08 pounds sodium
28 aluminate powder was added and the entire batch was mixed for 45 minutes prior to spray
29 drying in a 10 foot spray dryer using the conditions shown in Table 1.

32 Example 2

33 22.4 pounds of HiSil 233 (90% SiO₂, 10% H₂O) , 1.03 pounds of sodium aluminate
34 powder and 1.48 pounds of Versal 250 (75% Al₂O₃, 25% H₂O) was added to a 130 liter plow

01 shear mixer (Littleford type). The mixer was turned on and a solution made up of 17.8 pounds
02 of DI H₂O, 17.8 pounds of TEAOH (35 %) and 1.9 pounds of NaOH (50 %) was injected into
03 the mixer through a spray nozzle. The thick paste was mixed for 10 minutes and then without
04 discharging the initial material a second batch was made using the exact same mixing sequence.
05 The resulting thick paste was transferred from the Littleford mixer to a standard 30 gallon mix
06 tank containing 28 pounds of DI H₂O. The slurry was mixed for 1 hour at 2000 RPM prior to
07 spray drying in a 10 foot spray dryer using the conditions shown in Table 1.
08

09 Comparative Example A

10 10 grams of spray dried material from Example 1 was placed into three 45 ml Parr
11 bombs. The bombs were sealed and placed in an oven at 150° C for 24, 48 and 144 hours. After
12 the bombs were removed from the oven, they were cooled and the material was filtered and
13 washed with 100 cc of DI H₂O. All three samples were x-ray amorphous.
14

15 Comparative Example B

16 10 grams of spray dried material from Example 1 was placed in three 45 ml Parr bombs.
17 30 grams of DI H₂O was added to the Parr bombs. The bombs were sealed and placed in an
18 oven at 150° C for 24, 48 and 288 hours. After the bombs were removed from the oven, they
19 were cooled and the material was filtered and washed with 100 cc of DI H₂O. All three samples
20 were x-ray amorphous.
21

22 Comparative Example C

23 The slurry fed to the spray dryer in Example 1 had a pH of 12.2. The spray dried
24 material had a pH of 10.3. 15 grams of spray dried material from Example 1 was placed into a
25 125 ml Parr bomb. 60 grams of DI H₂O was added to the Parr bomb to form a slurry. The pH
26 of the slurry was increased to 12.3 by the addition of 2.4 gm of 25% NaOH. The Parr bomb
27 was sealed and placed in an oven at 150° C for 48 hours. The bomb was removed from the
28 oven, cooled and the material was filtered and washed with 100 cc of DI H₂O. The sample was
29 x-ray amorphous.
30

31 Comparative Example D

32 15 grams of spray dried material from Example 1 was placed into a 125 ml Parr bomb.
33 60 grams of DI H₂O was added to the Parr bomb to form a slurry. The pH of the slurry was
34

01 increased to 13.0 by the addition of 3.4 gm of 25% NaOH. The Parr bomb was sealed and
02 placed in an oven at 150° C for 48 hours. The bomb was removed from the oven, cooled and
03 the material was filtered and washed with 100 cc of DI H₂O. The sample was x-ray amorphous.

04 Comparative Example E

05
06 10 grams of spray dried material from Example 2 was placed into three 45 ml Parr
07 bombs. The bombs were sealed and placed in an oven at 150° C for 24, 48 and 144 hours. After
08 the bombs were removed from the oven, they were cooled and the material was filtered and
09 washed with 100 cc of DI H₂O. All the samples were x-ray amorphous.

10 Comparative Example F

11
12 10 grams of spray dried material from Example 2 was placed into two 45 ml Parr
13 bombs. 30 grams of DI H₂O was added to the Parr bombs. They were sealed and placed in an
14 oven at 150° C for 24 and 288 hours. After the bombs were removed from the oven, they were
15 cooled and the material was filtered and washed with 100 cc of DI H₂O. Both samples were x-
16 ray amorphous.

17 Comparative Example G

18
19 The slurry fed to the spray dryer in Example 2 had a pH of 12.5. The spray dried
20 material had a pH of 10.2. 15.6 grams of spray dried material from Example 2 was placed into a
21 125 ml Parr bomb. Sixty grams of DI H₂O was added to the Parr bomb to form a slurry. The
22 pH of the slurry was increased to 13.0 by the addition of 3.1 gm of 25% NaOH. The Parr bomb
23 was sealed and placed in an oven at 150° C for 48 hours. The bomb was removed from the
24 oven, cooled and the material was filtered and washed with 100 cc of DI H₂O. The sample was
25 x-ray amorphous.

26 Example 3

27 Adding Organic Template to the Spray Dried Material

28
29 10.8 gm of spray dried material from Example 1 was placed into two 45 ml Parr bombs.
30 30 gms of DI H₂O was added to each bomb and then 5.0 gm of 35% TEAOH solution was
31 added. The bombs were sealed and placed in an oven at 150° C for 24 and 48 hours. After the
32 bombs were removed from the oven, they were cooled and the material was filtered and washed
33
34

01 with 100 cc of DI H₂O. The 24 hour sample showed a small amount of crystalline zeolite beta.
02 The 48 hour sample was highly crystalline, phase pure beta.

03 Example 4

04 Adding Organic Template to the Spray Dried Material

05 10.8 gm of spray dried material from Example 2 was placed into two 45 ml Parr bombs.
06 30 grams of DI H₂O was added to each bomb and then 5.0 gm of 35% TEAOH solution was
07 added. The bombs were sealed and placed in an oven at 150° C for 26 and 48 hours. After the
08 bombs were removed from the oven, they were cooled and the material was filtered and washed
09 with 100 cc of DI H₂O. The 26 hour sample was partially crystalline zeolite beta. The 48 hour
10 sample was highly crystalline phase pure beta. Five grams of the crystalline sample was
11 slurried in 50 ml of DI H₂O containing 5 grams of ammonium nitrate. After 1 hour at 80° C the
12 sample was filtered, washed and dried at 105° C. The dried sample was placed in a muffle
13 furnace programmed to ramp to 550° C in 6 hours and hold at 550° C for 4 hours. The calcined
14 H-form beta had a N₂ BET surface area of 704 m²/g.
15

16 Example 5

17 196 pounds of DI H₂O and 3.8 pounds of NaOH (50 %) was added to a 100 gallon
18 Cowles dissolver. The mixer was turned on and 44.9 pounds HiSil 233 (90% SiO₂, 10% H₂O)
19 was added over 25 minutes. After the HiSil 233 addition was complete, 2.95 pounds of Versal
20 250 (75% Al₂O₃, 25% H₂O) and 2.08 pounds sodium aluminate powder was added and the
21 entire batch was mixed for 45 minutes prior to spray drying in a 10 foot spray dryer using the
22 conditions shown in Table 1.
23

24 Comparative Example H

25 35 gm of spray dried material from Example 5 was added to a solution consisting of 108
26 gm of DI H₂O and 35.1 gm of TEAOH (35 %). The thick slurry was poured into two Parr
27 bombs which were sealed and placed in an oven at 150° C for 47 and 71 hours. After the
28 bombs were removed from the oven, they were cooled and the material was filtered and washed
29 with 250 cc of DI H₂O. Both samples were x-ray amorphous.
30
31
32
33
34

TABLE 1
Spray Drying Conditions

<u>Example</u>	<u>Inlet Temp.</u>	<u>Outlet Temp.</u>	<u>Wheel</u>	<u>%</u>	PSD		
	<u>°F (°C)</u>	<u>°F (°C)</u>	<u>Speed</u>	<u>LOI*</u>	<u>d(v,0.5)</u>	<u>d(v,0.1)</u>	<u>d(v,0.9)</u>
1	600 (316)	260 (127)	11,500	30.5	120	47	219
2	600 (316)	250 (121)	11,500	26.7	90	35	199
12	610 (321)	250 (121)	12,000	10.9	109	49	201

* Loss on ignition

Table 2

Reaction Mixture (non-seeded) Stoichiometry (in moles)

<u>Example</u>	<u>1</u>	<u>2</u>	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>	<u>E</u>	<u>F</u>
SAR*	19.9	19.9	19.9	19.9	19.9	19.9	19.9	19.9
TEA / SiO ₂	0.13	0.13	0.13	0.13	0.13	0.13	0.13	0.13
OH / SiO ₂	0.23	0.23	0.23	0.23	0.33	0.37	0.23	0.23
Na / SiO ₂	0.11	0.11	0.11	0.11	0.21	0.25	0.11	0.11

01	H ₂ O / SiO ₂	0.64	0.35	0.64	17.1	22.8	22.9	0.35	13.3
02									
03									
04									
05									
06	Example	G	3	4	5	H	6	7	
07									
08	SAR	19.9	19.9	19.9	19.9	19.9	19.9	19.9	
09	TEA / SiO ₂	0.13	0.23	0.23	0.00	0.19	0.18	0.18	
10	OH / SiO ₂	0.34	0.34	0.33	0.11	0.29	0.29	0.29	
11	Na / SiO ₂	0.22	0.11	0.11	0.11	0.11	0.11	0.11	
12	H ₂ O / SiO ₂	19.5	17.5	16.3	0.47	16.5	15.6	15.6	
13									

*Silica/alumina mole ratio